

# Reduced density-matrix functionals from many-particle theory

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Received 10 February 2017 / Received in final form 20 March 2017  
Published online 10 July 2017

**Abstract.** In materials with strong electron correlation the proper treatment of local atomic physics described by orbital occupations is crucial. Reduced density-matrix functional theory is a natural extension of density functional theory for systems that are dominated by orbital physics. We review the current state of reduced density-matrix functional theory (RDMFT). For atomic structure relaxations or *ab-initio* molecular dynamics the combination of density functional theory (DFT) and dynamical mean-field theory (DMFT) possesses a number of disadvantages, like the cumbersome evaluation of forces. We therefore describe a method, DFT+RDMFT, that combines many-particle effects based on reduced density-matrix functional theory with a density functional-like framework. A recent development is the construction of density-matrix functionals directly from many-particle theory such as methods from quantum chemistry or many-particle Green's functions. We present the underlying exact theorems and describe current progress towards quantitative functionals.

## 1 Introduction

The *ab-initio* description of materials with strong electronic correlations is a standing challenge in solid state physics. The combination of density functional theory (DFT, [1,2]) with dynamical mean-field theory (DMFT, [3–6]), i.e. DFT+DMFT, has proven to be a successful route for the description of materials with strong electronic correlations.

However for the purpose of atomic structure relaxations, stability investigations and *ab-initio* molecular dynamics the existing DFT+DMFT schemes face two main issues: a cumbersome calculation of forces on atoms from linear response theory [7,8] and the computationally expensive solution of multi-orbital impurity problems. Furthermore it is clear that dealing with dynamical quantities, such as the electronic

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Green's function, is not necessary for the calculation of atomic forces. Thus a hybrid theory that combines DFT with a many-particle approach involving only static, i.e. frequency-independent, quantities is highly desirable.

Blöchl et al. [9] have proposed such a hybrid approach with the help of reduced density-matrix functional theory (RDMFT, [10–13]). RDMFT uses the one-particle reduced density matrix (1-RDM) as a natural variable and thus emphasizes orbital occupations. The approach is based on a variational total energy expression, which guarantees the efficient and consistent evaluation of forces using the Hellmann-Feynman theorem [14]. This also allows the use of very efficient Car-Parrinello molecular dynamics approach [15]. A double counting problem similar to DFT+DMFT does not arise within the proposed DFT+RDMFT scheme [9].

The first part of this publication (Sect. 2) reviews the current state of one-particle reduced density matrix functional theory. A more complete discussion can be found in a recent review by Pernal and Giesbertz [16]. In the review presented here we emphasize observations that point out the current challenges in this field. The second part, Section 3, describes our ideas and approaches to tackle these issues. We describe the DFT+RDMFT scheme and new approaches to approximate the density-matrix functional. New functionals are necessary, because despite the success of simple functionals within RDMFT, the most common density-matrix functionals reproduce a number of features in a qualitatively incorrect manner [17–19].

## 2 One-particle reduced density matrix functional theory

### 2.1 Hamiltonian and density matrices

The many-particle Hamiltonian for a system of  $N$  electrons that interact via a Coulomb potential and an external potential  $v_{\text{ext}}$ , can be expressed in an orthonormal one-particle basis  $\{\chi_\alpha(\mathbf{r}, \sigma)\}$  as

$$\hat{H} = \sum_{\alpha, \beta} h_{\alpha, \beta} \hat{c}_\alpha^\dagger \hat{c}_\beta + \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} U_{\alpha, \beta, \delta, \gamma} \hat{c}_\alpha^\dagger \hat{c}_\beta^\dagger \hat{c}_\gamma \hat{c}_\delta. \quad (1)$$

The creation and annihilation operators,  $\hat{c}_\alpha^\dagger$  and  $\hat{c}_\alpha$ , for an electron in spin-orbital  $\chi_\alpha$  obey the usual anticommutation relations.

The matrix elements of the one-particle Hamiltonian are defined as

$$h_{\alpha, \beta} = \sum_{\sigma} \int d^3\mathbf{r} \chi_\alpha^*(\mathbf{r}, \sigma) \left( \frac{-\hbar^2}{2m_e} \nabla^2 + v_{\text{ext}}(\mathbf{r}) \right) \chi_\beta(\mathbf{r}, \sigma) \quad (2)$$

and the interaction matrix elements as [20]

$$U_{\alpha\beta\gamma\delta} = \langle \alpha\beta | \gamma\delta \rangle = \sum_{\sigma, \sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{e^2 \chi_\alpha^*(\mathbf{r}, \sigma) \chi_\beta^*(\mathbf{r}', \sigma') \chi_\gamma(\mathbf{r}, \sigma) \chi_\delta(\mathbf{r}', \sigma')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

The main quantity for the solution of the quantum many-particle problem is the  $n$ -particle reduced density matrix  $\mathbf{D}^{(n)}$  ( $n$ -RDM). It is defined for an ensemble of fermionic many-particle wave functions  $|\Psi_i\rangle$  with probabilities  $P_i$  where  $0 \leq P_i \leq 1$  and  $\sum_i P_i = 1$  as

$$D_{\alpha_1, \dots, \alpha_n; \alpha'_1, \dots, \alpha'_n}^{(n)} = \sum_i P_i \langle \Psi_i | \hat{c}_{\alpha'_n}^\dagger \dots \hat{c}_{\alpha'_1}^\dagger \hat{c}_{\alpha_1} \dots \hat{c}_{\alpha_n} | \Psi_i \rangle. \quad (4)$$

All expectation values of one- and two-particle operators can be expressed with the 1-RDM  $D_{\alpha,\beta}^{(1)} = \sum_i P_i \langle \Psi_i | \hat{c}_\beta^\dagger \hat{c}_\alpha | \Psi_i \rangle$  and 2-RDM  $\mathbf{D}^{(2)}$ , especially the energy as

$$E = \sum_i P_i \langle \Psi_i | \hat{H} | \Psi_i \rangle = \sum_i P_i \langle \Psi_i | \hat{h} + \hat{W} | \Psi_i \rangle = \sum_{\alpha\beta} h_{\alpha,\beta} D_{\beta,\alpha}^{(1)} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\delta\gamma} D_{\gamma,\delta;\beta,\alpha}^{(2)}. \quad (5)$$

The eigenvalues  $f_i$  of the 1-RDM are named occupations and its eigenvectors  $|\phi_i\rangle$  natural orbitals [21].

## 2.2 Modern formalism of RDMFT

The main quantity of interest for an interacting many-particle problem is the grand potential given as

$$\Omega_{T,\mu}(\hat{h} + \hat{W}) = -k_B T \cdot \ln \left[ \text{Tr} \left\{ e^{-\frac{1}{k_B T} (\hat{h} + \hat{W} - \mu \hat{N})} \right\} \right], \quad (6)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\mu$  is the chemical potential and  $\hat{N}$  is the operator of the total particle number. Within reduced density-matrix functional theory [10–13, 22, 23] the grand potential is written as

$$\Omega_{T,\mu}(\hat{h} + \hat{W}) = \min_{\mathbf{D}^{(1)}: 0 \leq f_i \leq 1} \left\{ \text{Tr}[\mathbf{D}^{(1)}(\mathbf{h} - \mu \mathbf{1})] + F_T^{\hat{W}}[\mathbf{D}^{(1)}] \right\}. \quad (7)$$

The reduced density-matrix functional  $F_T^{\hat{W}}[\mathbf{D}^{(1)}]$  (RDMF) is a universal functional of the 1-RDM [10]. The minimization is performed over all ensemble-representable 1-RDMs  $\mathbf{D}^{(1)}$ . A density matrix is called an ensemble-representable  $n$ -RDM, if it can be represented according to equation (4) by an ensemble of fermionic many-particle wave functions  $|\Psi_i\rangle$  and probabilities  $P_i$ . The necessary and sufficient conditions for the ensemble-representability of an 1-RDM  $\mathbf{D}^{(1)}$  are hermiticity and that its eigenvalues  $f_i$  fulfill  $0 \leq f_i \leq 1$  [24].

If a 1-RDM is representable according to equation (4) with exactly one, i.e.,  $P_1 = 1$ ,  $N$ -particle wave function  $|\Psi\rangle$ , it is called pure-state  $N$ -representable. The pure-state  $N$ -representability conditions (generalized Pauli constraints) for the 1-RDM are only known explicitly for small systems even though a systematic construction has been given by Klyachko et al. [25]. The inclusion of the pure-state  $N$ -representability conditions in the minimization of equation (7) with approximate RDMFs has shown to improve the resulting energies [26].

Levy [12] and Valone [13] have shown that the RDMF can be obtained from a constrained minimization over an ensemble of orthonormal fermionic many-particle wave functions  $|\Psi_i\rangle$  with ensemble probabilities  $P_i$  obeying  $0 \leq P_i \leq 1$  and  $\sum_i P_i = 1$  as

$$F_T^{\hat{W}}[\mathbf{D}^{(1)}] = \min_{\{P_i, |\Psi_i\rangle\} \rightarrow \mathbf{D}^{(1)}} \left[ \sum_i P_i \langle \Psi_i | \hat{W} | \Psi_i \rangle + k_B T \sum_i P_i \ln(P_i) \right]. \quad (8)$$

Here we denote with  $\{P_i, |\Psi_i\rangle\} \rightarrow \mathbf{D}^{(1)}$  the set of ensembles with a given 1-RDM  $\mathbf{D}^{(1)}$  according to equation (4).

The RDMF is usually decomposed into four contributions [27–29]: The Hartree energy  $F_H^{\hat{W}}[\mathbf{D}^{(1)}]$ , Fock energy  $F_x^{\hat{W}}[\mathbf{D}^{(1)}]$ , an entropy contribution of a non-interacting

system  $F_T^{\hat{0}}[\mathbf{D}^{(1)}]$  and correlation energy  $F_{c,T}^{\hat{W}}[\mathbf{D}^{(1)}]$  as

$$F_T^{\hat{W}}[\mathbf{D}^{(1)}] = F_H^{\hat{W}}[\mathbf{D}^{(1)}] + F_x^{\hat{W}}[\mathbf{D}^{(1)}] + F_T^{\hat{0}}[\mathbf{D}^{(1)}] + F_{c,T}^{\hat{W}}[\mathbf{D}^{(1)}] \quad (9)$$

$$F_H^{\hat{W}}[\mathbf{D}^{(1)}] = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha,\beta,\delta,\gamma} D_{\delta,\alpha}^{(1)} D_{\gamma,\beta}^{(1)}, \quad (10)$$

$$F_x^{\hat{W}}[\mathbf{D}^{(1)}] = -\frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha,\beta,\delta,\gamma} D_{\gamma,\alpha}^{(1)} D_{\delta,\beta}^{(1)}, \quad (11)$$

$$F_T^{\hat{0}}[\mathbf{D}^{(1)}] = k_B T \cdot \text{Tr} \left[ \mathbf{D}^{(1)} \ln \mathbf{D}^{(1)} - (\mathbf{1} - \mathbf{D}^{(1)}) \ln (\mathbf{1} - \mathbf{D}^{(1)}) \right]. \quad (12)$$

The correlation energy  $F_{c,T}^{\hat{W}}[\mathbf{D}^{(1)}]$  contains contributions from interaction as well as from the entropy and has to be approximated.

### 2.3 Approximate functionals for RDMFT

This section discusses several approaches for the construction of approximate parametrized RDMF. A more complete discussion can be found in a recent review by Pernal and Giesbertz [16]. We start by listing important properties of the exact RDMF and discuss classification schemes for approximate RDMFs.

#### 2.3.1 Properties of the RDMF

The correlation contribution  $F_{c,T}$  is non-positive for positive two-particle interactions [30–32]. The RDMF is convex with respect to the 1-RDM [22,33], its value is invariant under unitary transformation of the one-particle basis and particle hole symmetric [34,35].

In the case of zero temperature  $T = 0$ , the exact RDMF in equation (8) is given by the 2-RDM  $\mathbf{D}^{(2),\min}$  of the ensemble of many-particle wave functions at the minimum analogously to equation (5) as

$$F_{T=0}^{\hat{W}}[\mathbf{D}^{(1)}] = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\delta\gamma} D_{\gamma,\delta;\beta,\alpha}^{(2),\min}. \quad (13)$$

An approximation of the RDMF is equivalent to an approximation of the 2-RDM  $D^{(2),\min}$  by  $D^{(2),\text{approx}}$  in equation (13). In this way more properties of the RDMF can be formulated implicitly by expressing them as properties of the approximate 2-RDM. The approximate 2-RDM should be hermitian, antisymmetric and ensemble or pure-state  $N$ -representable. The complete set of ensemble  $N$ -representability conditions of the 2-RDM  $\mathbf{D}^{(2)}$  were given by Mazziotti [36,37]. A set of necessary pure-state  $N$ -representability conditions for the 2-RDM are also known [38]. The 2-RDM should also obey the sum rule relating it to the given 1-RDM  $\mathbf{D}^{(1)}$  and fulfill relations to higher-order RDMs [39].

The exact RDMF is size-consistent [33]. Violations of size-consistency by approximations can lead to unphysical delocalization of electrons especially in molecular dissociation problems [40]. Approximations should additionally conserve the volume-extensivity, so that the homogeneous electron gas can be described properly [41,42]. Furthermore the spin constancy condition [17,43,44] is obeyed by the exact RDMF. Violations of the spin constancy lead to an unphysical description of fractional spin states and the static correlation problem [44,45].

### 2.3.2 Static and dynamic correlation

It has early been recognized [46,47], that DFT with existing local or semi-local functionals such as LDA- or GGA-functionals can properly describe dynamical electron-electron correlation, i.e., the instantaneous short-range repulsion of electrons. In contrast, static or non-dynamical correlation results from near-degeneracy effects due to strong interactions between ground and excited states. Dynamical correlation can be loosely related to the frequency-independent part of the electronic self-energy, while static correlation is related to the frequency-dependent contribution to the electronic self-energy [48].

### 2.3.3 Classification of approximate functionals

Approximate RDMFs can be classified according to which properties of the exact RDMF they obey or violate [27,41,49].

A different classification into explicit and implicit RDMFs considers the evaluation of the approximate RDMF for a given 1-RDM: explicit functionals are given explicitly in terms of the 1-RDM or occupations and natural orbitals. In contrast in the evaluation of implicit functionals a solution of some equations or a minimization problem is necessary.

Finally approximate functionals can also be classified according to which interaction matrix elements they depend on. This is done by transforming the expression of the approx. RDMF into the basis of natural orbitals  $|\phi\rangle$  and observing which of the transformed interaction matrix elements,

$$\tilde{U}_{i,j,k,l} = \sum_{\sigma,\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{e^2 \phi_i^*(\mathbf{r},\sigma) \phi_j^*(\mathbf{r}',\sigma') \phi_k(\mathbf{r},\sigma) \phi_l(\mathbf{r}',\sigma')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}, \quad (14)$$

contribute [41]. Most existing approximate functionals are JK-only in the sense that their expression in the basis of natural orbitals depends only on the Coulomb ( $J_{ij} = \tilde{U}_{i,j,i,j}$ ) and exchange ( $K_{ij} = \tilde{U}_{i,j,j,i}$ ) integrals [50]. Kollmar [51] has evaluated the best possible JK-only wave function, i.e., a wave function that leads to JK-only energy expression of the RDMF in terms of the corresponding 2-RDM. He has shown that the best possible JK-only wave function only gives about one third of the correlation energy for the water molecule at equilibrium configuration, even though it gives exact results for two-electron closed-shell cases. Furthermore he concludes that there can be no sufficiently accurate JK-only RDMF that also obeys the N-representability conditions for the 2-RDM. This is due to underestimated dynamic correlation of the pair-excited configuration interaction ansatz, that is related to the JK-only approximation [16]. For example a proper description of Van der Waals interactions requires the RDMF to include integrals beyond the JK-only approximation [52].

### 2.3.4 Müller-type functionals

The 2-RDM corresponding to the Hartree and Fock energy given in equation (10) and (11) can be written by using the occupations  $f_i$  and natural orbitals  $|\phi_i\rangle$  ( $\phi_i(\alpha) = \langle \chi_\alpha | \phi_i \rangle$ ) of the 1RDM as

$$D_{\text{HF},\alpha\beta;\gamma\delta}^{(2)} = \sum_{ij} f_i f_j \phi_i^*(\gamma) \phi_i(\alpha) \phi_j^*(\delta) \phi_j(\beta) - \sum_{ij} c_{\text{HF}}(f_i, f_j) \phi_i^*(\delta) \phi_i(\alpha) \phi_j^*(\gamma) \phi_j(\beta). \quad (15)$$

A large number of approximate functionals were constructed by employing a different function of occupations  $c(f_i, f_j)$  instead of the product  $c_{HF}(f_i, f_j) = f_i f_j$  in equation (15).

Müller [53] proposed the form  $c(f_i, f_j) = f_i^{1/2} f_j^{1/2}$ , which gives the exact ground-state energy for the half-filled Hubbard dimer [18, 54]. We have however shown that the Müller functional predicts an unphysical infinite magnetic susceptibility for the half-filled Hubbard dimer [19]. It is also known to overcorrelate [55–57]. Buijse and Baerends [54] later rederived the Müller functional starting from the exchange-correlation hole [58]. The development of Müller-type functionals of the form in equation (15) was furthered in three directions:

**Self-energy corrections:** Goedecker and Umrigar (GU, [59]) proposed to remove orbital self-interaction from the Müller functional by excluding terms with  $i = j$  from the summations in equation (15). This removal violates the sum rule relating the 1-RDM and 2-RDM. The GU-functional improves the description of small molecules at equilibrium geometries when compared to the Müller functional but can not describe the dissociation [57] and is size-inconsistent [40].

**Repulsive corrections:** Gritsenko et al. [60] proposed a series of repulsive corrections to the Müller functional to correct for its overcorrelating behaviour. The first two corrections called BBC1 and BBC2 distinguish between weakly and strongly occupied natural orbitals and modify  $c(f_i, f_j) = f_i^{1/2} f_j^{1/2}$  if both orbitals are either both weakly or both strongly occupied. BBC3 additionally distinguishes between bonding and antibonding orbitals. The difficulty to classify the orbitals has been addressed by Rohr et al. They have proposed an automatic variant of BBC3 called AC3, which introduces a damping function that smoothens the steps in the orbital classification [61]. An extensive benchmark of the BBCn-functionals for the G2-set of molecules [62, 63] resulted in deviations of atomization energies of BBC3 about three times larger than with second order Møller-Plesset perturbation theory (MP2) when compared to CCSD(T)<sup>1</sup> reference values [57].

**Empirical modifications of the occupation dependence  $c(f_i, f_j)$ :** The Marques-Lathiotakis functional (ML, [64]) uses a Padé approximant of order [1/1] for the occupation dependence  $c(f_i, f_j)$ , where the three parameters are obtained by a fit for a subset of the G2-database. The ML-functional is size consistent [40], but violates spin-constancy [17] and thus can not describe the dissociation properly [61]. The deviations of the correlations energies of the ML-functional for closed-shell molecules from the G2-set are only half of the corresponding BBC3 errors [64].

The power functional was proposed by Sharma et al. [65] to cure the overcorrelating behaviour of the Müller functional by an interpolation of the exponents in  $c(f_i, f_j) = f_i^\alpha f_j^\alpha$  with  $1/2 < \alpha < 1$  between the Müller limit  $\alpha = 1/2$  and the Hartree-Fock-limit  $\alpha = 1$ . The power functional can be rewritten as an explicit RDMF, thus making it size consistent. It violates the spin constancy condition, but can be forced to reproduce the correct dissociation energy by fitting the exponent  $\alpha$  [66]. Also by fitting the exponent, the deviations of the atomization energy and correlation energy from the power functional for molecules from the G2-set can be brought to the level of the BBC3 functional [66].

Due to the construction of the power functional by interpolation it inherits several problems from the limits [19]: We have shown that on the one hand it is missing

<sup>1</sup> Coupled cluster theory with full single and double excitations and perturbative treatment of triple excitations.

the derivative discontinuity of the energy at integer particle numbers like the Müller functional and that it on the other hand yields an unphysical transition to an anti-ferromagnetic state like the Hartree-Fock approximation. The power functionals also shows a plethora of unphysical non-collinear magnetic structures and transitions.

The power functional has been shown to yield good results for the bands gaps of simple semiconductors such as Ge or GaAs and simple transition metal oxides like NiO, MnO or FeO [65]. It should be noted here, that the band gap was estimated by an extrapolation technique [67] due to the missing derivative discontinuity. Applications to transition metal oxides investigated the parameter dependence [68,69] as well as metal-insulator transitions [70,71] and showed good agreement with other methods. However due to the antiferromagnetic ground state of the transition metal oxides under investigation, the pathologies of the power functional for the prediction of magnetic structures did not become apparent.

### 2.3.5 Natural orbital functionals from cumulant expansions

A second important class of functionals is derived from a cumulant expansion of the 2-RDM [72]

$$D_{\alpha\beta;\gamma\delta}^{(2)} = D_{\text{HF},\alpha\beta;\gamma\delta}^{(2)} + \gamma_{\alpha\beta;\gamma\delta}^{(2)}, \quad (16)$$

where the two-particle cumulant  $\gamma^{(2)}$  is approximated while imposing conditions that hold for the exact cumulant. Piris et al. proposed a series of natural orbital functionals called PNOFn ( $n = 1-6$ ) [73-75]. Starting from PNOF4 [76] the functionals in the series fulfill the hermiticity, antisymmetry and the (2,2)-positivity [36] conditions for the ensemble N-representability of the 2-RDM, also known as the D, Q and G-conditions.

One striking feature of the PNOF5 functional [77,78] is that it can also be derived from a generating many-particle wave function. This wave function is an antisymmetrized product of strongly orthogonal geminals (APSG, [79]) with parameters directly determined by the occupations of the 1-RDM. The knowledge of a generating wave function also allows the application of multiconfigurational perturbation theory [80,81]. Applications to the G2-set of molecules showed that this correction can recover part of the dynamical correlation that is underestimated in PNOF5 [82]. Approximations of the 2-RDM that explicitly try to respect the N-representability have also been proposed by Kollmar and Hess [51,83].

### 2.3.6 Functionals for model systems

The reduced complexity of model systems such as the single-impurity Anderson model [84] or single band Hubbard model [85-87] allows to relate the RDMF directly to degrees of freedom of the 1-RDM. Carlsson and Hennig related the interaction energy to the second moment of the 1-RDM [88,89] and successfully applied it to the three-dimensional Hubbard Hamiltonian and Anderson impurity models.

López-Sandoval and Pastor observed a pseudo-universal relation between the correlation energy and the nearest-neighbor 1-RDM elements for one-, two- and three-dimensional Hubbard models [90,91]. Combined with exact results for a Hubbard dimer, they constructed an approximate RDMF, that can describe the ground-state energy of one-, two- and three-dimensional Hubbard models [92,93] at different fillings and interactions strengths as well as charge excitation gaps very well.

The Hubbard dimer as a reference system is also used in the two-level approximation [94,95] for single impurity Anderson models by Töws et al. They employ a

unitary transformation of the bath basis states, that has been chosen to concentrate the effects of the bath to one bath site, and a subsequent truncation of all other bath states. Schade and Blöchl have recently proposed a generalization [96] of the two-level approximation, that can be systematically converged (see also Sect. 3.2).

### 2.3.7 Implicit functionals

The preceding sections covered ideas for the construction of explicit functionals. Implicit functionals include the solution of some equations or minimization problem. One of the first implicit functionals was proposed by Yasuda [35] and included the solution of Nakatsuji's density equations [97] together with the decoupling approximations for the 3- and 4-RDMs. Mazziotti restricted Levy's constrained search to antisymmetrized geminal power wave functions [98,99]. Other APSG-based implicit functionals have been proposed by Cioslowski et al. [50,100].

Kollmar and Hess [51,83,101] proposed to use a limited configuration expansion representation in Levy's constrained search equation (8), that only contains excitations from the HF-determinant of an electron pair consisting of two electrons of opposite spin from an occupied orbital to an unoccupied orbital. This results in a minimization problem for the pair-excitation coefficients to be solved.

Restrictions of the wave function in Levy's constrained search have the advantageous property of being variational in the sense that the resulting value of the RDMF is a guaranteed upper bound for the exact RDMF.

## 2.4 Extensions of the theory

### 2.4.1 Gaps and spectral information

Several physically interesting quantities can be directly obtained from RDMFT: grand canonical potential, expectation values of one-particle operators, equilibrium bond distances, dissociation curves, vibrational frequencies, etc. Properties like spectra or static response functions, like static dipole polarizabilities [102], however are not directly accessible. Several methods have been proposed to estimate photoemission spectra starting from Slater's transition state [70,103], local RDMFT [104,105] and approximations in terms of higher order RDMs [69]. Applications of these approaches to model systems [18,69] as well as real materials [69–71] showed mixed performances.

The missing derivative discontinuity of the energy at integer particle numbers in approximate RDMFs [106] as well as the non-existence of a Kohn-Sham system at zero temperature within RDMFT make the estimation of the fundamental gap a challenging problem. Helbig et al. proposed an extrapolation method [67] based on the chemical potential  $\mu = \partial E(N)/\partial N$  for fractional particle numbers  $N$ . Alternatively the gap could be read off from an approximated photoemission spectrum.

### 2.4.2 Hybrid theories

Local and semi-local DFT functionals are accurate at small interelectronic distances [46,47], but fail for systems with a poor balance between dynamical (short-range) and static (long-range) correlation. This suggests a range-separation of the electron-electron interaction and a treatment of the long-range component with methods that can describe static correlation [107–111]. Subsequently approximate RDMFT functionals have been used for the long-range part [112,113], thus establishing a hybrid DFT-RDMFT scheme.



### 2.4.3 Large scale calculations

One important consequence of the non-existence of a Kohn-Sham system in RDMFT at zero temperature is that the 1-RDM is the 1-RDM of the interacting system. The ensemble N-representability conditions for the 1-RDM are given in terms of the occupations, so it is advantageous to choose the occupations and natural orbitals as variational parameters. In principle every natural orbital could have a finite occupation and has to be considered. This is in sharp contrast to zero-temperature DFT, where the number of Kohn-Sham wave functions that have to be considered for a ground-state calculation is proportional to the number of electrons in the system. During minimization within RDMFT, equation (7), the natural orbitals have to be kept orthonormal. Thus the minimization over orbitals in RDMFT is the main computational bottleneck. An extensive discussion of approaches to mediate this problem can be found in the review by Pernal and Giesbertz [16].

## 3 DFT+RDMFT

### 3.1 General ideas

Our work rests on a general framework of integrating RDMFT into DFT calculations, which is based on an additive augmentation [9]

$$E_{\text{DFT+RDMFT}} = E_{\text{DFT}} + \left( F_{\text{xc,RDMFT}} - F_{\text{xc,DFT}} \right), \quad (17)$$

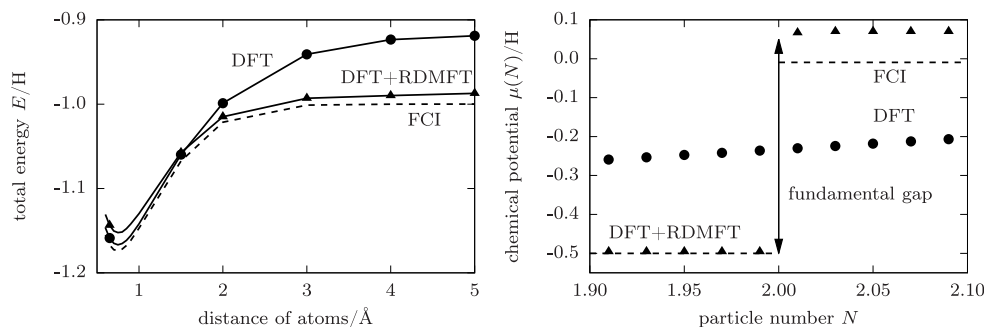
where the second part,  $\Delta F = F_{\text{xc,RDMFT}} - F_{\text{xc,DFT}}$ , is a correction to the exchange-correlation energy. This correction has the form of an interaction energy and a corresponding double-counting term. When the same approximations are applied to both terms of the correction, the scheme profits from error cancellation. This approach provides a consistent and unambiguous definition of the double counting term.

The approximations are three-fold: Firstly, the Kohn-Sham wave functions of the density functional calculation are projected onto a local-orbital basis set to provide access to the machinery of orbital-based many-particle methods. Analogous to dynamical mean-field theory, we secondly truncate the interaction matrix elements that connect separate clusters, where a cluster is typically made up from all local orbitals tied to one atom. Finally, the RDMF  $F_{\text{xc,RDMFT}}$  is decomposed into a sum of atomic contributions. Each of these terms represents an impurity problem. The impurity problem is an extended system with an interaction limited to a specific atomic site.

Note, that the decomposition done on the level of a RDMF differs from similar approximations done in terms of the one-particle Hamiltonian. Even though the interaction is limited, the electron correlations extend into the environment.

Additional approximations can be applied on top of the ones mentioned. A specific approximation of this kind is our local hybrid functional PBE0r, which approximates the RDMF in the correction  $\Delta F$  by a scaled Fock energy. The calculations on real systems provide confidence into the mapping onto local orbitals.

The quality of the decomposition of RDMF into sum of atomic (cluster) contributions described above has been explored for Hubbard chains [9], because exact results are readily produced. The method has proven to cope well with the static correlation problem. The spin correlations are well described and the proper singlet ground state is obtained. However the derivative discontinuities of the energy at integer particle numbers are washed out for intermediate interaction strengths.



**Fig. 1.** Left panel: dissociation curve within non-spin-polarized DFT+RDMFT (solid line with triangles). The local basis for the RDMF was chosen as one s-orbital located at each atom and the RDMF was evaluated numerically exact. The results are compared to non-spin-polarized DFT (solid line with circles) and FCI results in the cc-pVQZ basis [114] with Orca [115] (dashed line). PBE [116] was chosen as the DFT xc-functional. Right panel: chemical potential  $\mu = \partial E(N)/\partial N$  for the stretched hydrogen molecule ( $d = 5 \text{ \AA}$ ).

### 3.2 Adaptive cluster approximation

After the RDMF  $F_{xc,RDMFT}$  has been decomposed into atomic contributions, several RDMFs have to be evaluated for impurity problems. The impurity problem is an infinite system with a interaction limited to a specific site. To make the problem tractable a cluster approximation is required. In order to minimize the resulting errors, Schade and Blöchl have proposed the adaptive cluster approximation (ACA, [96]).

The ACA introduces a unitary transformation of the one-particle basis which turns the 1-RDM into a band matrix with minimal bandwidth. In the transformed density matrix the impurity orbitals are only connected to an inner bath with at most as many orbitals as the impurity itself. The cluster truncation errors can be controlled by increasing the number of blocks considered. The ACA is thus a generalization of the two-level approximation by Töws et al. [94,95].

Calculations have been performed for a number of models [96]. They indicate that the RDMF in the ACA converges rapidly to the exact result with the number of blocks considered.

### 3.3 RDMFs from many-particle wave functions

The deficiencies of explicit RDMFs [19] discussed earlier suggest to explore implicit functionals. Implicit functionals provide a solid basis for including static correlation effects and they hold promise to provide new ideas for the development of new explicit functionals.

Schade and Blöchl have succeeded to implement a constrained search solver that can treat configuration interaction expansions of many-particle wave functions in Levy's and Valone's constrained search formalism, equation (8), with up to  $5 \times 10^7$  Slater determinants on a desktop machine. The solver is based on the primal Powell-Hestenes augmented Lagrangian [117,118] and is formulated with sparse matrix-vector multiplications as basic operations. The implementation can either be used to calculate the numerically exact RDMF for up to 28 spin-orbitals or together with an iterative expansion of the space of Slater determinants for much larger systems.

Figure 1 shows results of the DFT+RDMFT scheme for the dissociation curve and chemical potential of the hydrogen molecule  $H_2$ . The DFT-part is implemented in the

projector augmented-wave formalism [119] and one s-state located at each atom was used as a local basis for the RDMF. The RDMF has been solved numerically exact by the constrained search solver described above. These calculations excluded the approximations due to the decomposition of the RDMF.

The overestimation of the total energy in the dissociation limit by a non-spin polarized DFT calculation, shows the static correlation error of approximate DFT functionals. This static correlation problem is cured by DFT+RDMFT, which yields a dissociation curve in good agreement with results from high-level quantum chemistry methods, albeit at a much lower cost. The DFT+RDMFT calculation also describes the derivative discontinuity of the energy and consequently also the fundamental gap correctly. It should be emphasized, that no unphysical breaking of the spin symmetry is necessary to obtain the correct energy in the dissociation limit. The symmetry breaking dilemma of HF or DFT calculations is a topic of intense discussions [44, 120–122].

### 3.4 Green's function based RDMFs

Blöchl et al. [123] have derived an exact relation between the RDMF  $F_T^{\hat{W}}[\mathbf{D}^{(1)}]$  and the Green's function functional, namely the Luttinger-Ward functional  $\Phi^{\hat{W}}[\mathbf{G}]$  [124].

This exact link provided by Blöchl et al. [123], sets the stage for the construction of approximate RDMFs based on well established many-body perturbation [125] and related methods. It can be written as

$$\begin{aligned}
 F_T^{\hat{W}}[\mathbf{D}^{(1)}] = & F_T^{\hat{0}}[\mathbf{D}^{(1)}] + \text{stat}_{\mathbf{h}'} \text{stat}_{\mathbf{G}, \boldsymbol{\Sigma}} \left\{ \Phi_{\beta}^{\hat{W}}[\mathbf{G}, \hat{W}] \right. \\
 & - \frac{1}{\beta} \sum_{\nu} e^{i\hbar\omega_{\nu}\beta 0^+} \text{Tr} \left\{ \ln \left[ \mathbf{1} - \bar{\mathbf{G}}(i\omega_{\nu}) \left( \mathbf{h}' + \boldsymbol{\Sigma}(i\omega_{\nu}) - \bar{\mathbf{h}} \right) \right] \right. \\
 & \left. \left. + \left( \mathbf{h}' + \boldsymbol{\Sigma}(i\omega_{\nu}) - \bar{\mathbf{h}} \right) \mathbf{G}(i\omega_{\nu}) - \left[ \mathbf{G}(i\omega_{\nu}) - \bar{\mathbf{G}} \right] \left( \mathbf{h}' - \bar{\mathbf{h}} \right) \right\} \right\}, \quad (18)
 \end{aligned}$$

where the first terms is the entropy of a non-interacting system  $F_T^{\hat{0}}[\mathbf{D}^{(1)}]$  given in equation (12). The single-particle Matsubara Green's function is denoted by  $\mathbf{G}(i\omega_{\nu})$  and  $\boldsymbol{\Sigma}(i\omega_{\nu})$  is the corresponding self-energy.  $\beta$  denotes the inverse temperature  $\beta = 1/(k_B T)$ . The Luttinger-Ward functional  $\Phi^{\hat{W}}[\mathbf{G}]$  is a universal functional of Green's function and is defined as an infinite sum of closed and connected skeleton diagrams [124]. The non-interacting Hamiltonian  $\bar{\mathbf{h}}[\mathbf{D}^{(1)}] = \mu \mathbf{1} + \frac{1}{\beta} \ln \left[ (\mathbf{1} - \mathbf{D}^{(1)}) / (\mathbf{D}^{(1)}) \right]$  is a direct functional of 1-RDM and the non-interacting Green's function corresponding to  $\bar{\mathbf{h}}$  is given by

$$\bar{\mathbf{G}}(i\omega_{\nu}) = \left( (i\hbar\omega_{\nu} + \mu) \mathbf{1} - \bar{\mathbf{h}} \right)^{-1}. \quad (19)$$

The 1-RDM constraint  $\mathbf{D}^{(1)} = \frac{1}{\beta} \sum_{\nu} e^{i\hbar\omega_{\nu}\beta 0^+} \mathbf{G}(i\omega_{\nu})$  in the stationary point evaluation in equation (18), is enforced using the Lagrange multiplier  $\mathbf{h}'$ .

The exact relation in equation (18) requires a stationary point search in the space of Green's functions and the self-energies as well as the fulfillment of the 1-RDM constraints. But nevertheless, it allows to construct approximations in a controlled way through well known methods in the field of many-body perturbation theory. A related perturbation theory for the RDMF based on Green's functions was proposed by Baldsiefen et al. [29].

We propose a two step approximate scheme which leads to an algebraic expression of the RDMF  $F_T^{\hat{W}}[\mathbf{D}^{(1)}]$  as follows [126].

1. Define a mapping of the form,  $\mathbf{D}^{(1)} \rightarrow \mathbf{G}[\mathbf{D}^{(1)}]$ , which provides a Green's function  $\mathbf{G}[\mathbf{D}^{(1)}]$  for a given 1-RDM  $\mathbf{D}^{(1)}$ , such that the 1-RDM constraints are fulfilled. This circumvents the stationary point searches and leads to

$$F_{\beta}^{\hat{W}}[\mathbf{D}^{(1)}] \approx F_T^{\hat{0}}[\mathbf{D}^{(1)}] + \Phi_{\beta}^{LW}[\mathbf{G}[\mathbf{D}^{(1)}], \hat{W}] - \frac{1}{\beta} \sum_{\nu} e^{i\hbar\omega_{\nu}\beta 0^{+}} \times \text{Tr} \left\{ \ln [\bar{\mathbf{G}}(i\omega_{\nu})\mathbf{G}^{-1}(i\omega_{\nu})] + \bar{\mathbf{G}}^{-1}(i\omega_{\nu})\mathbf{G}(i\omega_{\nu}) - \mathbf{1} \right\}. \quad (20)$$

2. The second approximation is introduced in the evaluation of the Luttinger-Ward functional  $\Phi_{\beta}^{LW}[\mathbf{G}[\mathbf{D}^{(1)}], \hat{W}]$  for a given Green's function  $\mathbf{G}[\mathbf{D}^{(1)}]$ : the Luttinger-Ward functional is evaluated through a perturbation expansion in the interaction strength. Here, one can make use of well known conserving approximations that originated from the theory proposed by Baym and Kadanoff [127], like Hartree-Fock or fluctuation-exchange [128].

### 3.4.1 Mapping to Green's function

The simplest mapping from a 1-RDM to a Green's function, that reproduces the 1-RDM, is given by equation (19). This simple mapping however leads to the breakdown of the perturbation expansion at low temperatures [126].

The construction of mappings, that avoid the collapse of the perturbation theory, is tackled through the spectral function  $\mathbf{A}(\epsilon)$ . We restrict the spectral function to a set of  $N$  poles

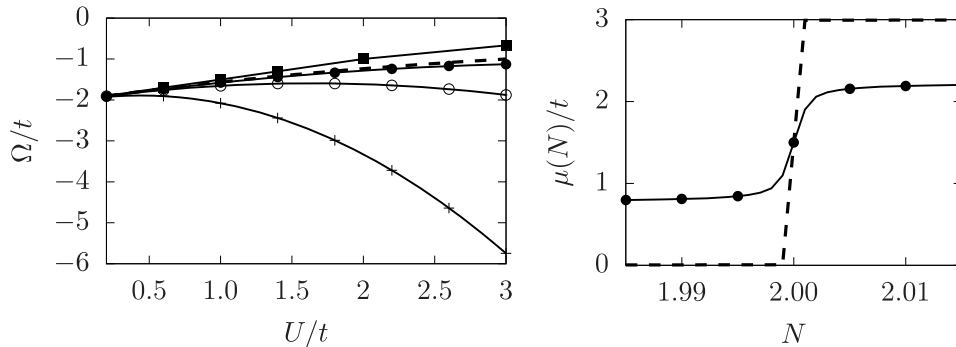
$$A_{\alpha\beta}(\epsilon) = \sum_n \langle \chi_{\alpha} | \phi_n \rangle \langle \phi_n | \chi_{\beta} \rangle \sum_{i=1}^N w_i(f_n) \delta(\epsilon - \lambda_i(f_n)). \quad (21)$$

The weights  $w_i$  and positions of the poles  $\lambda_i$  are functions of the occupations  $f_i$  and are chosen such that the Green's function fulfills the 1-RDM constraints. The complexity can be varied by using different number of poles  $N$  in the description of the Green's function. The simplest non-trivial Green's function has two poles and constitutes the two-pole approximation.

### 3.4.2 Performance of the two-pole approximation

In this section we use the approximate RDMF  $F_{\beta}^{\hat{W}}[\mathbf{D}^{(1)}]$  of equation (20) with the two-pole model Green's function. The Luttinger-Ward functional for the given two-pole Green's function is approximated up to second order in the perturbation. This is formulated within Hugenholtz diagrammatics [129] and contains the HF-diagram and the so called bubble or tadpole diagram as well as its corresponding exchange diagram.

The grand canonical potential of the half-filled Hubbard dimer resulting from this approximate RDMF is shown in Figure 2 as a function of the interaction strength  $U/t$ . The energies obtained from the approximate density-matrix functional are underestimated. It is also noticeable from Figure 2, that by increasing the pole-separation  $\Delta$ , the approximate density-matrix functional leads to better estimation of the grand potential. The value of the free parameter  $\Delta$  can be fixed by performing a stationary point search in the space of pole-separation [126].



**Fig. 2.** Left panel: the grand canonical potential for the half-filled Hubbard dimer as a function of interaction strength  $U/t$  for different approximations of RDMFs. Dashed line: exact result. Solid squares: Hartree-Fock approximation. Approximate RDMF of equation (20) with  $\Delta/t = 1.8$  (solid circles),  $\Delta/t = 0.8$  (open circles) and  $\Delta/t = 0.2$  (crosses). Right panel: chemical potential  $\mu(N)$  of the Hubbard dimer with  $U = 3t$  as function of particle number  $N$ . Same convention for symbols as the figure in left panel. The value of inverse temperature is  $\beta = 1000/t$ .

As evident from Figure 2, the approximate density-matrix functional of equation (20) fails to reproduce the derivative discontinuity of the total energy at integer particle numbers. It nevertheless produces a smoothed derivative discontinuity (the chemical potential undergoes a continuous transition between two linear functions). Thereby, using the extrapolation method proposed by Helbig et al. [67], one can estimate the band-gap.

## 4 Summary

We have reviewed the current state of reduced density-matrix functional theory as an approach to describe strong electronic correlations. The main challenge is to derive approximations of the RDMF, that on the one hand cover static and dynamic correlation, and on the other hand can be systematically improved and evaluated efficiently. We survey the existing approaches to approximate the RDMF and show, that even simple approximations can properly describe static correlations, while dynamical correlations are challenging for existing approximate RDMFs.

We describe a hybrid DFT-RDMFT scheme, named DFT+RDMFT, where the DFT description of local atomic physics is corrected by a RDMF functional. Together with a local approximation this scheme is expected to cover local correlation effects similar to DFT+DMFT, while providing a straight-forward and efficient way to calculate forces for structure relaxations and ab-initio molecular dynamics. We show results for the full dissociation curve of the hydrogen molecule, that show that static correlation is indeed well described in this hybrid scheme.

For larger systems the RDMF has to be approximated, because of the exponentially growing complexity of the many-particle problem. We show a systematic way to construct a smaller effective system for the approximation of the RDMF within the local approximation, named adaptive cluster approximation.

Finally we describe the connection between the RDMF, the Luttinger-Ward functional and Green's functions, illustrate a route to use this connection to derive new systematic approximations to the RDMF from many-body perturbation theory and show results for Hubbard systems.

We are deeply saddened by the loss of our dear colleague Thomas Pruschke. We would like to express our gratitude for his unflagging support as a colleague and his invaluable contributions as a physicist to this and other projects. We gratefully acknowledge support of the Deutsche Forschungsgemeinschaft through FOR 1346.

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## References

1. P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964)
2. W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965)
3. A. Georges, G. Kotliar, Phys. Rev. B **45**, 6479 (1992)
4. V.I. Anisimov, A.I. Poteryaev, M.A. Korotin, A.O. Anokhin, G. Kotliar, J. Phys.: Condens. Matter **9**, 7359 (1997)
5. A.I. Lichtenstein, M.I. Katsnelson, Phys. Rev. B **57**, 6884 (1998)
6. G. Kotliar, S.Y. Savrasov, K. Haule, V.S. Oudovenko, O. Parcollet, C.A. Marianetti, Rev. Mod. Phys. **78**, 865 (2006)
7. S.Y. Savrasov, G. Kotliar, Phys. Rev. Lett. **90**, 056401 (2003)
8. I. Leonov, V.I. Anisimov, D. Vollhardt, Phys. Rev. Lett. **112**, 146401 (2014)
9. P.E. Blöchl, C.F.J. Walther, T. Pruschke, Phys. Rev. B **84**, 205101 (2011)
10. T.L. Gilbert, Phys. Rev. B **12**, 2111 (1975)
11. R.A. Donnelly, R.G. Parr, J. Chem. Phys. **69**, 4431 (1978)
12. M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979)
13. S.M. Valone, J. Chem. Phys. **73**, 1344 (1980)
14. R.P. Feynman, Phys. Rev. **56**, 340 (1939)
15. R. Car, M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985)
16. K. Pernal, K.J.H. Giesbertz, Top. Curr. Chem. **368**, 125 (2016)
17. N. Helbig, G. Theodorakopoulos, N.N. Lathiotakis, J. Chem. Phys. **135**, 054109 (2011)
18. S. Di Sabatino, J.A. Berger, L. Reining, P. Romaniello, J. Chem. Phys. **143**, 024108 (2015)
19. E. Kamil, R. Schade, T. Pruschke, P.E. Blöchl, Phys. Rev. B **93**, 085141 (2016)
20. A. Szabo, N. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, 2012)
21. P.O. Löwdin, Phys. Rev. **97**, 1474 (1955)
22. E.H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983)
23. P.W. Ayers, S. Golden, M. Levy, J. Chem. Phys. **124**, 054101 (2006)
24. A.J. Coleman, Rev. Mod. Phys. **35**, 668 (1963)
25. M. Altunbulak, A. Klyachko, Commun. Math. Phys. **282**, 287 (2008)
26. I. Theophilou, N.N. Lathiotakis, M.A.L. Marques, N. Helbig, J. Chem. Phys. **142**, 154108 (2015)
27. N. Helbig, Ph.D. thesis, Freie Universität Berlin, 2006
28. P.E. Blöchl, T. Pruschke, M. Potthoff, Phys. Rev. B **88**, 205139 (2013)
29. T. Baldsiefen, A. Cangi, E.K.U. Gross, Phys. Rev. A **92**, 052514 (2015)
30. E.H. Lieb, Phys. Rev. Lett. **46**, 457 (1981)
31. E.H. Lieb, Phys. Rev. Lett. **47**, 69 (1981)
32. T. Baldsiefen, Ph.D. thesis, Freie Universität Berlin, 2012
33. R. Erdahl, V. Smith, *Density Matrices and Density Functionals: Proceedings of the A. John Coleman Symposium* (1987)
34. C. Valdemoro, Phys. Rev. A **45**, 4462 (1992)
35. K. Yasuda, Phys. Rev. A **63**, 032517 (2001)
36. D.A. Mazziotti, Phys. Rev. Lett. **108**, 263002 (2012)

37. D.A. Mazziotti, Phys. Rev. A **85**, 062507 (2012)
38. D.A. Mazziotti, Phys. Rev. A **94**, 032516 (2016)
39. B.C. Carlson, J.M. Keller, Phys. Rev. **121**, 659 (1961)
40. N.N. Lathiotakis, N.I. Gidopoulos, N. Helbig, J. Chem. Phys. **132**, 084105 (2010)
41. J. Cioslowski, K. Pernal, P. Ziesche, J. Chem. Phys. **117**, 9560 (2002)
42. J. Cioslowski, K. Pernal, J. Chem. Phys. **120**, 10364 (2004)
43. W. Yang, Y. Zhang, P.W. Ayers, Phys. Rev. Lett. **84**, 5172 (2000)
44. A.J. Cohen, P. Mori-Sánchez, W. Yang, J. Chem. Phys. **129**, 121104 (2008)
45. A.J. Cohen, P. Mori-Sánchez, W. Yang, Science **321**, 792 (2008)
46. D.C. Langreth, J.P. Perdew, Phys. Rev. B **15**, 2884 (1977)
47. K. Burke, J.P. Perdew, Int. J. Quantum Chem. **56**, 199 (1995)
48. G. Kotliar, Electronic Structure of Correlated Materials: Slave-Boson Methods and Dynamical Mean-Field Theory, in *DMFT at 25: Infinite Dimensions*, edited by E. Pavarini, E. Koch, D. Vollhardt, A. Lichtenstein (2014)
49. C.L. Benavides-Riveros, J.C. Várilly, Eur. Phys. J. D **66**, 274 (2012)
50. J. Cioslowski, K. Pernal, M. Buchowiecki, J. Chem. Phys. **119**, 6443 (2003)
51. C. Kollmar, J. Chem. Phys. **121**, 11581 (2004)
52. L.M. Mentel, X.W. Sheng, O.V. Gritsenko, E.J. Baerends, J. Chem. Phys. **137**, 204117 (2012)
53. A. Müller, Phys. Lett. A **105**, 446 (1984)
54. M.A. Buijse, E.J. Baerends, Mol. Phys. **100**, 401 (2002)
55. G. Csányi, T.A. Arias, Phys. Rev. B **61**, 7348 (2000)
56. N.N. Lathiotakis, N. Helbig, E.K.U. Gross, Phys. Rev. B **75**, 195120 (2007)
57. N.N. Lathiotakis, M.A.L. Marques, J. Chem. Phys. **128**, 184103 (2008)
58. J.C. Slater, Phys. Rev. **81**, 385 (1951)
59. S. Goedecker, C.J. Umrigar, Phys. Rev. Lett. **81**, 866 (1998)
60. O. Gritsenko, K. Pernal, E.J. Baerends, J. Chem. Phys. **122**, 204102 (2005)
61. D.R. Rohr, K. Pernal, O.V. Gritsenko, E.J. Baerends, J. Chem. Phys. **129**, 164105 (2008)
62. L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, J. Chem. Phys. **106**, 1063 (1997)
63. L.A. Curtiss, P.C. Redfern, K. Raghavachari, J.A. Pople, J. Chem. Phys. **109**, 42 (1998)
64. M.A.L. Marques, N.N. Lathiotakis, Phys. Rev. A **77**, 032509 (2008)
65. S. Sharma, J.K. Dewhurst, N.N. Lathiotakis, E.K.U. Gross, Phys. Rev. B **78**, 201103 (2008)
66. N.N. Lathiotakis, S. Sharma, J.K. Dewhurst, F.G. Eich, M.A.L. Marques, E.K.U. Gross, Phys. Rev. A **79**, 040501 (2009)
67. N. Helbig, N.N. Lathiotakis, M. Albrecht, E.K.U. Gross, EPL **77**, 67003 (2007)
68. Y. Shinohara, S. Sharma, S. Shallcross, N.N. Lathiotakis, E.K.U. Gross, J. Chem. Theory Comput. **11**, 4895 (2015)
69. S. Di Sabatino, J.A. Berger, L. Reining, P. Romaniello, Phys. Rev. B **94**, 155141 (2016)
70. S. Sharma, J.K. Dewhurst, S. Shallcross, E.K.U. Gross, Phys. Rev. Lett. **110**, 116403 (2013)
71. Y. Shinohara, S. Sharma, J.K. Dewhurst, S. Shallcross, N.N. Lathiotakis, E.K.U. Gross, New J. Phys. **17**, 093038 (2015)
72. W. Kutzelnigg, D. Mukherjee, J. Chem. Phys. **110**, 2800 (1999)
73. M. Piris, P. Otto, Int. J. Quantum Chem. **94**, 317 (2003)
74. M. Piris, Int. J. Quantum Chem. **113**, 620 (2013)
75. M. Piris, J.M. Ugalde, Int. J. Quantum Chem. **114**, 1169 (2014)
76. M. Piris, J.M. Matxain, X. Lopez, J.M. Ugalde, J. Chem. Phys. **133**, 111101 (2010)
77. M. Piris, X. Lopez, F. Ruipérez, J.M. Matxain, J.M. Ugalde, J. Chem. Phys. **134**, 164102 (2011)
78. M. Piris, J.M. Matxain, X. Lopez, J. Chem. Phys. **139**, 234109 (2013)
79. K. Pernal, Comp. Theor. Chem. **1003**, 127 (2013)
80. Z. Rolik, A. Szabados, P.R. Surján, J. Chem. Phys. **119**, 1922 (2003)
81. M. Piris, J. Chem. Phys. **139**, 064111 (2013)

82. M. Piris, F. Ruipérez, J. Matxain, *Mol. Phys.* **112**, 1 (2014)
83. C. Kollmar, B.A. Hess, *J. Chem. Phys.* **120**, 3158 (2004)
84. P. Anderson, *Phys. Rev.* **124**, 41 (1961)
85. M.C. Gutzwiller, *Phys. Rev. Lett.* **10**, 159 (1963)
86. J. Hubbard, *Proc. R. Soc. London A* **276**, 238 (1963)
87. J. Kanamori, *Prog. Theor. Phys.* **30**, 275 (1963)
88. A.E. Carlsson, *Phys. Rev. B* **56**, 12058 (1997)
89. R.G. Hennig, A.E. Carlsson, *Phys. Rev. B* **63**, 115116 (2001)
90. R. López-Sandoval, G.M. Pastor, *Phys. Rev. B* **61**, 1764 (2000)
91. M. Saubanère, G.M. Pastor, *Phys. Rev. B* **79**, 235101 (2009)
92. R. López-Sandoval, G.M. Pastor, *Phys. Rev. B* **66**, 155118 (2002)
93. R. López-Sandoval, G.M. Pastor, *Phys. Rev. B* **69**, 085101 (2004)
94. W. Töws, G.M. Pastor, *Phys. Rev. B* **83**, 235101 (2011)
95. W. Töws, G.M. Pastor, *Phys. Rev. B* **86**, 245123 (2012)
96. R. Schade, P.E. Blöchl, arXiv:1612.06692 (2016)
97. H. Nakatsuji, *Phys. Rev. A* **14**, 41 (1976)
98. D.A. Mazziotti, *J. Chem. Phys.* **112**, 10125 (2000)
99. D.A. Mazziotti, *Chem. Phys. Lett.* **338**, 323 (2001)
100. J. Cioslowski, M. Buchowiecki, P. Ziesche, *J. Chem. Phys.* **119**, 11570 (2003)
101. C. Kollmar, B.A. Hess, *J. Chem. Phys.* **119**, 4655 (2003)
102. K. Pernal, E.J. Baerends, *J. Chem. Phys.* **124**, 014102 (2006)
103. D.A. Liberman, *Phys. Rev. B* **62**, 6851 (2000)
104. N.N. Lathiotakis, N. Helbig, A. Rubio, N.I. Gidopoulos, *Phys. Rev. A* **90**, 032511 (2014)
105. N.N. Lathiotakis, N. Helbig, A. Rubio, N.I. Gidopoulos, *J. Chem. Phys.* **141**, 164120 (2014)
106. N. Helbig, N.N. Lathiotakis, E.K.U. Gross, *Phys. Rev. A* **79**, 022504 (2009)
107. H. Stoll, A. Savin, *Density Functionals for Correlation Energies of Atoms and Molecules* (Springer US, Boston, MA, 1985), pp. 177–207
108. A. Savin, *Int. J. Quantum Chem.* **34**, 59 (1988)
109. T. Leininger, H. Stoll, H.J. Werner, A. Savin, *Chem. Phys. Lett.* **275**, 151 (1997)
110. J. Toulouse, F.m.c. Colonna, A. Savin, *Phys. Rev. A* **70**, 062505 (2004)
111. E. Goll, H.J. Werner, H. Stoll, *Phys. Chem. Chem. Phys.* **7**, 3917 (2005)
112. K. Pernal, *Phys. Rev. A* **81**, 052511 (2010)
113. D.R. Rohr, J. Toulouse, K. Pernal, *Phys. Rev. A* **82**, 052502 (2010)
114. T.H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989)
115. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73 (2012)
116. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
117. M. Powell, A method for nonlinear constraints in minimization problems, in *Optimization* (Academic Press, NY, 1969), pp. 283–298
118. M.R. Hestenes, *J. Optim. Theory Appl.* **4**, 303 (1969)
119. P.E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994)
120. J.P. Perdew, A. Ruzsinszky, L.A. Constantin, J. Sun, G.I. Csonka, *J. Chem. Theory Comput.* **5**, 902 (2009)
121. A.J. Cohen, P. Mori-Sánchez, W. Yang, *Chem. Rev.* **112**, 289 (2012)
122. J.P. Perdew, A. Savin, K. Burke, *Phys. Rev. A* **51**, 4531 (1995)
123. P.E. Blöchl, T. Pruschke, M. Potthoff, *Phys. Rev. B* **88**, 205139 (2013)
124. J.M. Luttinger, J.C. Ward, *Phys. Rev.* **118**, 1417 (1960)
125. G. Mahan, *Many-Particle Physics, Physics of Solids and Liquids* (Springer, 2000)
126. E. Kamil, Ph.D. thesis, University of Göttingen, 2016
127. G. Baym, *Phys. Rev.* **127**, 1391 (1962)
128. N.E. Bickers, D. Scalapino, *Ann. Phys.* **193**, 206 (1989)
129. J. Negele, H. Orland, *Quantum many-particle systems* (1988)